Pseudo wastewater treatment by combining adsorption and phytoaccumulation on the *Acrostichum aureum* Linn. plant/activated carbon system

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Abstract

In this study, the pseudo wastewater containing Zn, Fe, Cu ions was clean-up by a combination of physical adsorption onto activated carbon medium and phytoaccumulation using *Acrostichum aureum* Linn. plants. The adsorption capability of the activated carbon for the Fe, Cu, and Zn ions was 3.05, 3.72, and 2.85 mg·g−1, respectively, at the saturation. The phytoaccumulation performance was proved by analyzing the individual residual ash collected after pyrolysis up to 1000 C of the leaf, stem, and root of the plants. Thermal analyses of thermogravimetry data showed that the weight of the residual ash of the phytoremediated leaf, stem, and root of the plants was 37.0, 19.0, and 65.7 wt.%, respectively. Energy-dispersive X−ray spectroscopy determined the amount of Fe element in the residual ash of phytoremediated root is 7.05 wt.%, while that of the initial root is 1.18 wt.%. Conclusively, it can be proved that combining physical and biological processes is feasible to treat wastewater containing metal ions.

Keywords: Phytoaccumulation, activated carbon, wastewater, *Acrostichum aureum* Linn., adsorption.

1. Introduction

The excessive release of heavy metals into the environment via general industrial and agricultural activities [2] is one reason for the pollution of water and soil [3]. When the exposed amount of heavy metals is above the permissible limits of humans, they may risk the health conditions. Excess of copper (Cu) ions may disrupt homeostasis and cause disease conditions associated with the hepatic disorder and neurodegenerative alteration. [1]. Free iron can donate or accept an electron from neighboring molecules to damage cellular components that are toxic to the cell [4]. Compared to Cu, Fe ions, zinc is relatively harmless. The accumulation of free zinc at high doses results in a consequence of ischemia or trauma [29]. So far, several technologies, such as precipitation [5], membrane filtration [6−12], ion exchange [13−16], adsorption over other media [17−20], and co−precipitation/adsorption [21], have been employed to clean-up wastewater. Among these methods, the adsorption onto activated carbon (AC) has been considered as a highly effective technique for the removal of heavy metals from wastewater [30]. However, the challenge is to achieve a reasonably long service life of AC because of saturation over time. Therefore, securing a long enough life cycle of AC is a crucial bottleneck for the potential implementation of the ion adsorption method in purifying wastewater containing heavy metal species. A system combining AC medium and plants can resolve the current challenging issue regarding enhancing the service cycle of AC material. This system can be considered a combination of phytoremediation and adsorption to remove (or reduce) heavy metal species in wastewater.

In Vietnam, as a country located in the tropical zone, mangrove forests are widely prevailing. The root system of mangrove trees (e.g., *Acrostichum aureum* Linn., *Neem, Peepal, Maize, Ulmus, Araucaria heterophylla*) develops a strong and dominant single main root that grows vertically into the ground without any critical restriction. The trees grow well on various substrates, including soil, sediment, or char [23]. In addition, the mangrove trees show the ability to uptake heavy metal ions through their root system and store the ions in complexes in various plant compartments [24]. Among these plants, *Acrostichum aureum* Linn. (AAL), which is a fern of brackish parts of tropical mangrove swamps and grows along the coastal belt in Vietnam [25], has been considered in phytoremediation in some publications. Dipu Sukumaran *et al.* [26] evaluated the phytoremediation capability of AAL in the treatment of shrimp farm effluent and investigated that the parameters including Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Nitrate (NO_3^-) were significantly reduced during thirty days of the experimental period. Another publication [27] experimentally proved that AAL can be applied for the phytoremediation of antibiotic−contaminated sediments. Particularly, a study, by Kaewtubtim *et al.* [28] on the storage of heavy metals in various parts (leaf, stem, and root) of AAL plants growing in Pattani Bay, Thailand, reported that the amounts of Cu, Zn, Ni, Mn, Cr, Pb metals ($mg \cdot kg^{-1}$) in AAL stems were measured to be 23.4, 25.1, 21.6, 3.7, 19.1, 6.3 $mg \cdot kg^{-1}$, respectively, while their amounts in AAL roots were higher as 41.5, 28.4, 24.3, 23.5, 29.3 and 22.1 $mg \cdot kg^{-1}$. These metals were not detected in AAL leaves. These results confirmed the accumulation and storage of metal ions in the AAL plants, which demonstrated the potential use of AAL plants in phytoremediation of heavy metals contaminated wastewater.

In this study, we designed a system of AAL plants grown in activated carbon (AC), evaluated the performance of the AAL/AC system in cleaning up pseudo wastewater containing Fe, Cu, and Zn ions with a particular concentration. The study aims to demonstrate a potential combination of physical and biological processes of remediation. The AC plays the role of growing medium and heavy−metal ion adsorber, and the AAL plants selectively accumulate throughout the phytoextraction.

2. Materials and methods

Determine the adsorption capacity of the AC

The AC, which is a commercial product made in Vietnam, was prepared in cylindrical granules with dimensions of diameter, 0.5 cm, and average length, 1.5 cm, as shown in Figure 1a. The main characteristics of the AC are as follows: the chemical compositions of C 32.3, O 44.7, Al 5.8, Si 13.1 wt.% and other minor elements; the point of zero charges in the range of 8.4 − 8.7; the surface area of 54.4 $m^2 \cdot g^{-1}$.

The pseudo wastewater was formed by dissolving $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$, and $CuSO_4 \cdot 5H_2O$ salts (Aldrich Chemical Co.,) in distilled water. The initial concentration of Fe, Cu, and Zn ions in the pseudo wastewater was determined to be 465 $mg \cdot L^{-1}$, 420 mg $\cdot L^{-1}$, 309 $mg \cdot L^{-1}$, respectively, measured using Photometer 7100 (Palintest, USA) instrument. The use of a reagent containing an alkaline thioglycolate reduces ferric iron to ferrous iron, the concentration of iron in solution is therefore named Fe^{2+}.Fe^{2+}.

40 g AC was introduced to 400 mL pseudo wastewater, continuously stirred, and stably kept at 30 ºC. By the hour, 2 mL of solution was taken out, filtered through a polytetrafluoroethylene (PTFE) syringe filter (0.45 μm pore size). Then, 1 mL of this filtered solution was diluted with 99 mL distilled water (total 100 mL solution) and measured Fe, Cu, and Zn concentration via the Photometer 7100 instrument, sequentially.

The concentrations of Fe, Cu, and Zn ions adsorbed onto the AC were calculated as follows:

$$q_t = \frac{(C_o - C_t) \times V}{D} \ (mg \cdot g^{-1}) \qquad \text{(Eq. 1)}$$

where,

C_o is the initial concentration of sorbate ($mg \cdot L^{-1}$)

C_t is the remaining concentration of sorbate in solution at any time t ($mg \cdot L^{-1}$)

q_t is the amount of sorbate adsorbed onto the AC at any time t ($mg \cdot g^{-1}$)

V is the initial volume of the solution (0.4 L in this study)

D is the AC dosage of 40 g.

Duplicates were performed for each sample and the relative standard error is equal or less than 3 %.

The AC was used as both nutrient−providing growing medium and heavy−metal ion adsorber. The adsorption capacity of the AC, which is defined as a stored mass (mg) of ions per unit mass (g) of AC, was determined by monitoring changes in ion mass of the heavy metals.

Design the system of AAL plants in the AC (named as the AAL/AC system)

AAL plants, which were collected from Can Gio mangrove forests in Ho Chi Minh City, Vietnam, have an average length of 50 cm and their leaves with an average size of 2x15 cm^2.

Plastic cylinder vases with dimensions of diameter, 13 cm, and height, 40 cm were used to contain the AAL/AC system. The solution volume was 2000 mL, and the initial weight of AC was 1600 g. These vases were connected with small plastic semi−transparent tubes to easily observe liquid−level inside the vase (Figure 1b). We experimented with ten same vases in the same condition, and randomly chose three vases to measure independently.

(a) (b)

Figure 1: The photographs of (a) the AC and (b) the AAL plants are grown in the AC

Evaluate the suitability of the AAL/AC system

The AAL plants grown in the AC were observed every day. Every three days, an appropriate solution (containing 50 mg·L^{-1} for NH_4^+ and 50 mg·L^{-1} for NO_3^-) was introduced to the system to supply water and nutrients for the plants, which mimics the natural environments and to maintain the liquid level inside the vase. After two months, it was evidenced that the plants grew well, and all leaves were green in healthy conditions with their average length ranging in 25−30 cm, which indicates the plants could steadily grow in the experimental conditions.

The plants were taken out of the vases, and then both the AAL and AC were washed in distilled water to leave out wastes produced during the initial two−month growth. A part of the AAL roots was cut and saved to use as a role of the initial root, which is to be compared with phytoremediated roots grown in pseudo wastewater. Then the AAL plants were grown in the AC again.

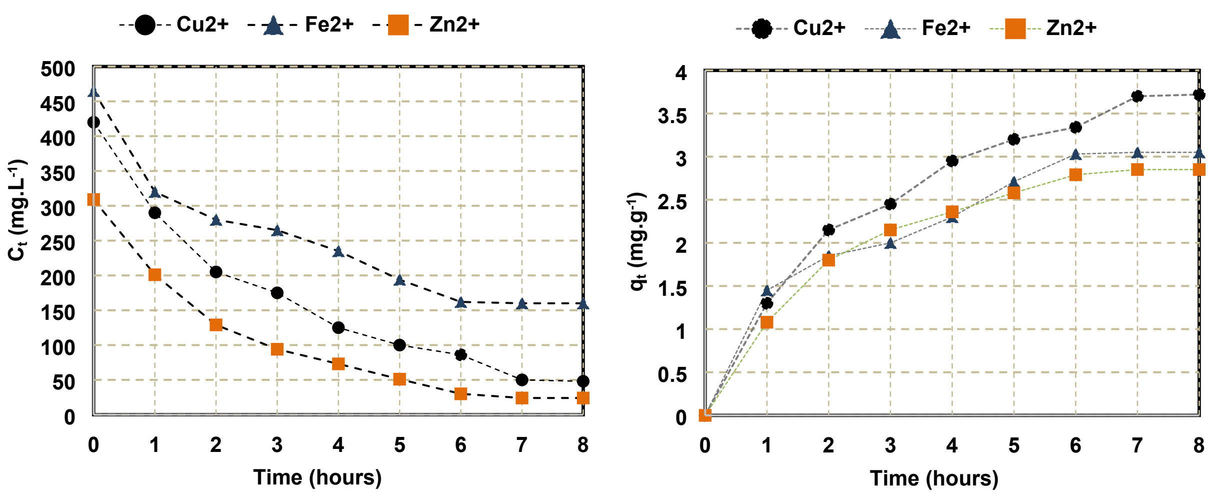
Evaluate the efficiency of the AAL/AC system on phytoremediation in pseudo wastewater

The pseudo wastewater was introduced into the AAL/AC system. The concentrations of metal ions in the system were continuously monitored using a multi−parameter photometer (Palintest 7100, USA). It must noted that the NH_4^+ and NO_3^- ions in the wastewater do not affect the measurements of the heavy metal cations of Fe^{2+}, Cu^{2+}, and Zn^{2+}.

After a month, all the concentrations of ions were completely down to zero. Then, the plants were taken out of the AC to precisely determine the types and amounts of the elements which were stored in various parts of the plants. The plants were divided into three individual parts of the root, branch (stem) and leaf. These parts were dried at 100 ºC in a drying oven for one day, then milled into a powder. TGA/DSC analysis (SETERAM, Labsys Evo, TG−DSC 1600°C) was made on the parts of root, stem, and leaf to investigate the thermal behavior of the compounds containing carbon in the plants. The samples were placed in a platinum cylindrical crucible and heated from 30 to 1000 ºC at a ramping rate of 10 K min^{-1} using a flow of N_2 (99.99%). The amount of each sample used for the measurements was constant at 28 mg. The compositions of the residual ashes after TGA/DSC were determined using EDX (Horiba H−7593, England).

3. Results and discussion

To objectively evaluate the adsorption performance of the AC (by itself, not the AAL/AC system), the metal ion concentrations in the pseudo wastewater were monitored, and the results are shown in Figure 2.

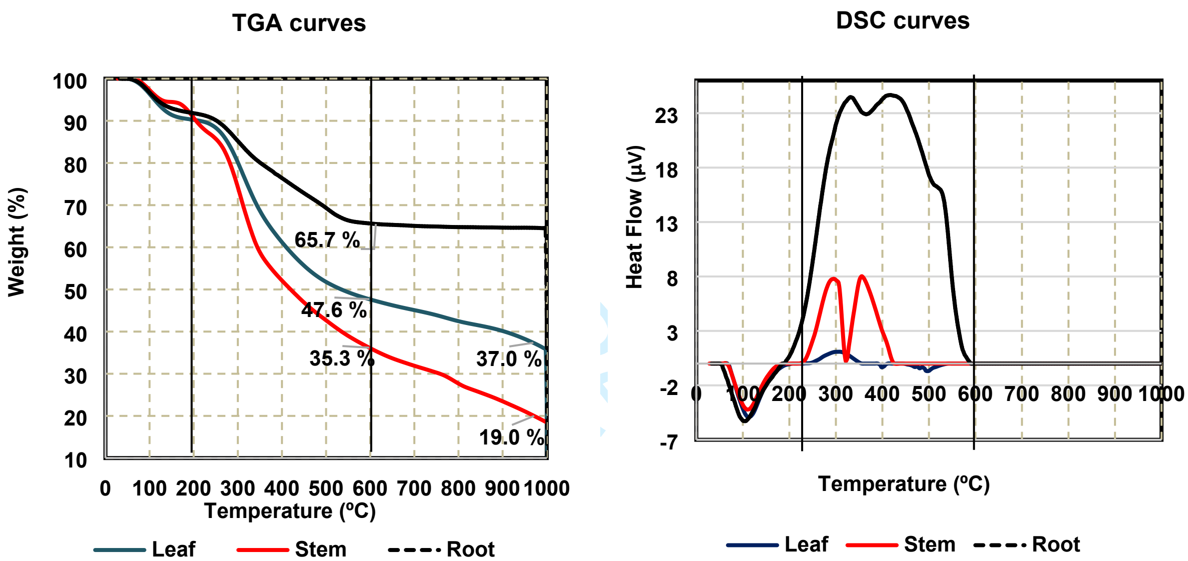


C_t vs. t (b) q_t vs. t

Figure 2: (a) A change in concentration (C_t) of Fe, Cu, Zn ions in solution as a function of time (b) The amount of the metal ions (q_t) adsorbed onto the AC with time

Figure 2a displays a change in concentration of each ion in the solution: the concentrations decrease slowly and lead to a constant value (i.e., saturation) after approximately 7 hours. Overall, 65.6 %, 88.1 %, and 92.2 % of Fe, Cu, and Zn ions, respectively, were adsorbed into the AC with respect to their initial concentration. These results in Figure 2a and Equation (1) were used to determine the adsorption capacity of the AC, which is defined as a stored mass (mg) of ions per unit mass (g) of adsorber (i.e., AC in this study). In Figure 2b, the storing capacities of AC for the Fe, Cu, and Zn ions were determined to be 3.05, 3.72, 2.85 mg·g^{-1}, respectively, at the saturation (i.e., at ~ 7 hours). The significance of the results are two−fold: (1) the overall adsorption performance of the AC for Fe, Cu and Zn ions is promisingly high for potential use in phytoremediation, and (2) according to the determined heavy–metal storing capacities (3.05 mg·g^{-1} for Fe; 3.72 mg·g^{-1} for Cu; 2.85 mg·g^{-1} for Zn), the initial AC weight (1600 g), consequently, has high maximum capabilities to store the heavy−metal Fe, Cu, Zn ions of 4880, 5952, 4560 mg, respectively.

The phytoremediation performance of the AAL/AC system was experimentally evaluated in the pseudo wastewater (containing the initial concentration of Fe, Cu, and Zn ions of 465 $mg \cdot L^{-1}$, 420 mg $\cdot L^{-1}$, 309 $mg \cdot L^{-1}$, respectively). To investigate the storage capability of each individual group of the AAL plants (i.e., root, stem and leaf) for the heavy−metal ions and other inorganic elements, TGA/DSC measurements were made on, and the results are shown in Figure 3. In order to exclude the effect of oxidation on the plants due to the presence of O_2, the measurements were performed in an inert gas condition with N_2.



(a) (b)

Figure 3: (a) TGA curves and (b) DSC curves of the individual parts of the AAL plants after used in phytoremediation

The TGA curves in Figure 3a reveal the weight change (%) with respect to the initial weight, while the DSC curves in Figure 3b indicate the exothermic and endothermic processes during the pyrolysis of the AAL leaf, stem and root parts in N_2 at temperatures from 25 to 1000 ºC. The first weight loss of the three samples starts at around 80 ºC and ends at approximately 130 ºC (Figure 3a), and, correspondingly, the endothermic peaks are shown in Figure 3b, which are ascribed to the vaporization of water from lignocellulose fibers [31]. At 200 °C, the weight loss of the AAL leaf, stem, and the root is similar – around 10 wt.% loss for all the groups. However, the thermal behaviors of the three groups become significantly different at a temperature from 200 ºC to 600 ºC. The total weight loss (initial 100% – residual ash wt.% remaining at 600 ºC) of the AAL leaf, stem, and root at 600 ºC was found to be 52.4, 64.7, and 34.3 wt.%, respectively (Figure 3a). Correspondingly, Figure 3b shows the DSC curve of the root sample with a large overlap of exothermic peaks which is attributed to full pyrolysis of compounds containing carbon (such as cellulose, hemicellulose, lignin or other compounds [32,33]), while the DSC curves of the leaf and stem specimens display smaller exothermic peaks due to incomplete organic pyrolysis. At temperatures higher than 600 ºC, no significant weight loss is observed in the root TGA curve, which is consistent with the DCS results in Figure 3b, where no endothermic or exothermic peaks are seen. The TGA curves of the leaf and stem samples, however, show a monotonic decrease in weight at temperatures higher than 600 ºC. As a result, the weight of the residual ash of AAL leaf, stem, and root at 1000 ºC was measured to be 37.0, 19.0, and 65.7 wt.%, respectively. These significant differences in weight after pyrolysis between the parts of AAL plants is likely attributed to the different amounts of inorganic compounds (in either form of oxides or salts) in each part that is thermally stable up to 1000 ºC during pyrolysis. Therefore, we hypothesize that the different weights of the parts after pyrolysis pertain to the absorption characteristics of the AAL plant – i.e., according to the high weight % remaining in the root, the AAL root may absorb different species from those absorbed by the AAL leaf and stem.

To precisely determine the types of elements in the residual ash after pyrolysis, EDX measurements were made in the three groups of phytoremediated samples and apart from the initial root. To compare the elemental compositions of the phytoremediated root, the initial root (non−phytoremediated) was also investigated with EDX. The results are shown in Table 1 and Figure 4.

Table 1: The components (wt.%) of the residual ashs

Element	Leaf	Stem	Root (phytoremediation)	Root (initial)
C K	44.36	35.73	–	27.18
O K	31.14	31.42	50.95	40.93
Na K	5.31	7.40	–	1.04
Mg K	1.59	1.11	0.94	–
Al K	–	0.71	10.67	7.92
Si K	9.58	8.72	28.62	20.40
P K	0.32	–	–	–
S K	0.61	0.34	–	–
Cl K	2.53	3.98	–	–
K K	2.47	7.15	1.77	1.25
Ca K	2.08	3.44	–	–
FeK	–	–	7.05	1.18

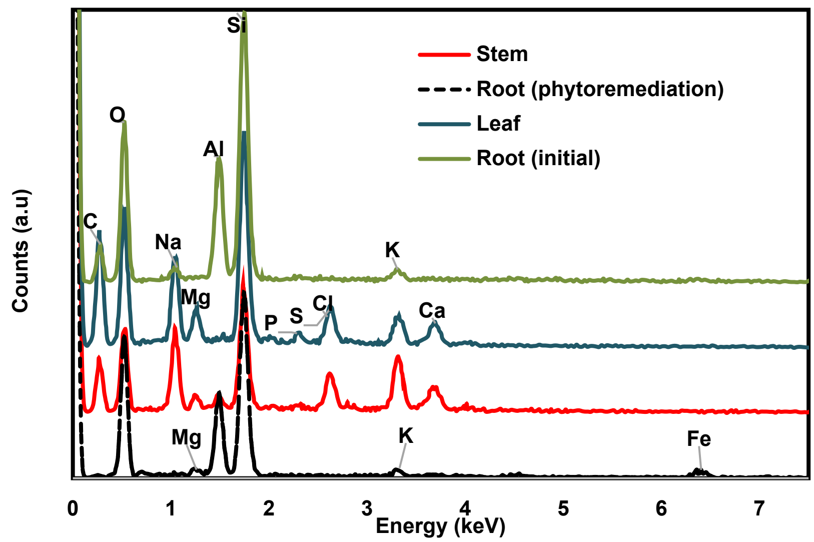


Figure 4: EDX spectra of the residual ashes of leaf, stem and roots (initial and phytoremediated)

In Table 1, the residual ashes from the leaf and stem contain very similar elements including Na, Mg, Si, S, Cl, K, Ca at similar concentrations (except the minor concentration of P for leaf and Al for stem) while the phytoremediated root is found to be significantly different from those of the leaf and stem. The concentrations of Al, Fe, and Si elements in the phytoremediated root are considerably higher than those in the leaf and stem residual ashes. Since the initial root naturally contains Al and Si elements at high concentrations, 7.92 wt.% for Al and 20.40 wt.% for Si, the elemental analysis for phytoremediation root serves as evidence that the roots of AAL plants selectively take up Fe ions. No carbon is detected in the phytoremediated root, unlike the high amounts of carbon, 44.36 wt.% for leaf and 35.73 wt.% for the stem. This result is due to the full pyrolysis of organic compounds containing carbon in the phytoremediated root, which is in good agreement with the TGA/DSC results in Figure 3. Frequently, the role of Al and Si for pyrolysis exhibits when these elements belong to the crystalline structure of zeolite (e.g., ZSM-5) or silicate alumina materials as catalytic carriers. However, in the current study, Al and Si elements are in separated oxides, not in crystals of zeolite. Therefore, it is hypothesized that the demonstrated full pyrolysis is likely facilitated by the catalytic effect of Fe in the phytoremediated root. The hypothesis is supported by several previous reports in the literature where similar results of significantly reduced carbon compounds are shown due to the impregnation of Fe [34-36]. Further studies of the Fe catalytic performance for pyrolysis are underway.

In order to objectively assess the phytoremediation ability of the system suggested in this study, it is required to determine the origin of Fe in the root: either naturally available or formed during phytoremediating process. To answer the question, the thermal behavior of the initial root (non−phytoremediated) was investigated, and the resulting TGA/DSC curves are presented in

Figure 5 to compare the thermal behaviors with those of phytoremediated root shown in Figure 3. The component comparison of the two residual ash samples (phytoremediated vs. initial) is also available from the EDX results in Figure 4 and Table 1: the amount of Fe element in the residual ash of phytoremediated root is 7.05 wt.%, while that of the initial root is 1.18 wt.%.

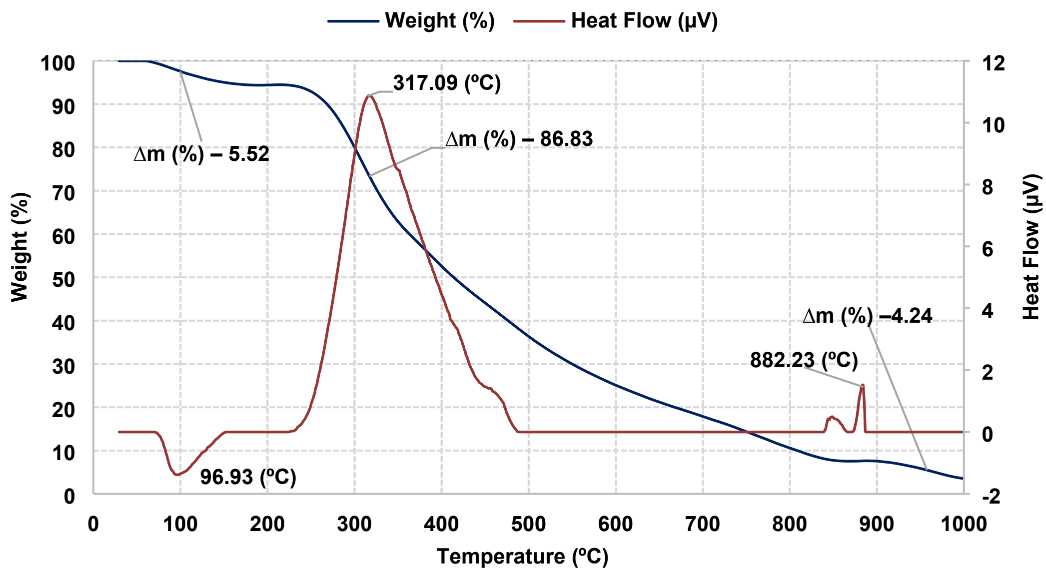


Figure 5: TGA/DSC curves of the initial root

The initial root's DSC curve in Figure 5 also has an endothermic peak at 96.93 ºC ascribed to the vaporization of water (as shown in the phytoremediated root), exothermic peaks ranging in 230 to 500 ºC, 840 to 865 ºC and 870 to 890 ºC attributed to the charring process of organic compounds. The TGA curve shows three steps of weight loss (with the values at the first, second, and third steps are 5.5, 86.8, and 4.2 wt.%, respectively), and the total amount of residual ash is below 5 wt.%. In Figure 3a, the weight of residual ash from the phytoremediated root is kept constantly at temperatures higher than 600 ºC (65.7 wt.%, without carbon). However, in the left axis of Figure 5, the weight of the initial root at 600 ºC is approximately 25 wt.% and continuously decreases to 5 wt.% (of which the carbon concentration is 27.18 wt% (Table 1)) at 1000 ºC. Therefore, similar to the leaf and stem's thermal behavior, the TGA and EDX results investigate the incomplete organic pyrolysis of the initial root. On the other hand, Table 1 shows the amount of Fe in the phytoremediated root is six times higher than that in the initial root, while Cu and Zn are not detected. It is deduced that the amount of Fe in the root is formed via the phytoremediation process, while the accumulation of Cu, Zn ions cannot be determined.

4. Conclusion

To demonstrate a potential combination of physical and biological processes of remediation, we designed the AAL plant/AC system, independently determined the AC's adsorption capacity, and proved the AAL plants' phytoremediation in the system. The results showed that the AC could play the role of growing medium and of a metal ion adsorbent thanks to its appropriate adsorption capacity (3.05 mg·g−1 for Fe, 3.72 mg·g−1 for Cu, and 2.85 mg·g−1 for Zn). The AAL plants grow well in the AC medium, selectively accumulate Fe ions in the roots, which was detected via EDX and TGA/DSC techniques. However, these techniques cannot detect Cu and Zn ions in the leaf, stem, and roots. We claim that almost metal ions were adsorbed and stored in the AC medium. The inexpensive and eco−friendly AAL/AC system is appropriate to many developing and underdeveloped countries that suffer from water contaminated by metal ions such as Cu, Zn, Fe.

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